

Cathodoluminescence Properties of In₂O₃-coated Y₂O₃:Eu³⁺ Phosphors

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Europium-doped Y₂O₃ phosphor (Y₂O₃:Eu³⁺) is a red phosphor that has been used in low-pressure fluorescence lamp, cathode ray tube (CRT) displays, and plasma display panels (PDPs) because of its characteristic sharp and hypersensitive luminescence.¹⁻³ Y₂O₃:Eu³⁺ exhibits a charge transfer excitation peaking at 242 nm and produces a strong 610-nm emission from Eu³⁺ with a narrow bandwidth attributed to the ⁵D₀ → ⁷F₂ transition.⁴⁻⁶ The quantum yield of this emission varies from 60 to 74% depending on the porosity of the Y₂O₃:Eu³⁺ particle.⁷ Recently, this phosphor has attracted a great deal of attention for use in field emission displays (FEDs), since it is presumed to be inherently stable under electron beam excitation.⁸⁻¹² Most studies on the cathodoluminescence (CL) properties of Y₂O₃:Eu³⁺ were conducted at accelerating voltages lower than 10 kV, although carbon nanotubes (CNTs), which are currently being investigated as electron field emitters for FEDs, require an applied voltage greater than 10 kV for reliable luminance.^{13,14} Ntwacaborwa and co-workers¹⁵ found that the CL intensity of Y₂O₃:Eu³⁺ was significantly reduced by exposure to an electron beam. In contrast to the sulfide phosphors, Y₂O₃:Eu³⁺ is an insulator with a bandgap energy of 6.0 eV. Electron irradiation of insulating materials builds a surface charge and creates a non-luminescent "dead layer" at the surface. Yamamoto and co-workers¹⁶ found that the current must be increased to regain the desired CL intensity and that the emission appeared primarily at edges or rims of grooves or holes made on the phosphor screen. The surface of Y₂O₃:Eu³⁺ can be coated with metal oxides, such as SiO₂, MgO and Al₂O₃ to alleviate this problem.^{17,18} However, the CL data of Y₂O₃:Eu³⁺ collected up to 4 kV showed that the resulting energy loss reduced the CL intensity. For FED applications, this problem can be solved by using a mixture of conductive materials such as In₂O₃, ZnO and SnO₂ with an insulating phosphor. For low-voltage FEDs, In₂O₃ was found most effective in this regard.^{19,20} In the current study, a Y₂O₃:Eu³⁺ surface was coated with In₂O₃ using two different deposition methods and the effects of the coating on the CL intensity was investigated as a function of accelerating voltages up to 17 kV. The findings revealed that the morphology of the In₂O₃ coating played a key role in determining the CL intensity.

Experimental

The In₂O₃ coating was fabricated using a precursor solution composed of InCl₃ in ethanol or water. The phosphor was added to 50 mL of ethanol or 10 mL of water in which various

concentrations of InCl₃ had been dissolved. After adjusting to pH 10 with a NH₄OH solution, the solutions were stirred for 1 h. The aqueous mixtures were heated at 70 °C to ensure the precipitation of In(OH)₃ onto the surface of the phosphor. The mixtures were then dried at 40 °C and heated in a box furnace at 400 °C for 3 h to convert indium hydroxide to indium oxide.

Phase information and surface morphology of the coated phosphors were determined by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). XRD data were collected on a D/Max-2000 diffractometer (Rigaku, Tokyo, Japan) with a graphite monochromator and Cu K α radiation (λ = 0.1541 nm). SEM micrographs and EDS spectra were acquired with a JSM-7000F FE-SEM (JEOL, Tokyo, Japan).

For the CL measurements, the uncoated and coated phosphors were deposited on glass using a screen printing method. A binder was prepared by dissolving ethyl cellulose (5 wt %) in α -terpineol and heating at 70 ~ 80 °C for 2 h. The phosphors were mixed with the binder in 10:6 weight ratio and cast onto the glass surface using a YP-450HP printer (Yuil, Seoul, Korea). The cast phosphors were annealed applying a two-step heating process: 280 °C for 2 h and 460 °C for 1 h. The thickness of the cast phosphor layer was approximately 10 μ m. The CL intensity was measured with a BM-7 Luminance Colorimeter (Topcon, Japan) as a function of the electron acceleration voltage at a current density of 3 μ A cm⁻² under a high vacuum (5.0 \times 10⁻⁶ torr) using an electron gun (PSI, Suwon, Korea). Photoluminescence (PL) spectra were also measured with an ARC 0.5 m Czerny-Turner monochromator equipped with a cooled Hamamatsu R-933-14 photomultiplier tube.

Results and Discussion

Morphology and phase. Fig. 1 shows the surface morphology of uncoated and In₂O₃-coated Y₂O₃:Eu³⁺ after annealed at 400 °C for 2 h. With the exception of some adhered particles, the surface of the uncoated phosphor was smooth and clean. The surface morphology of the phosphor that had been treated with 1 and 3 wt % of InCl₃ in ethanol was almost the same as that of the untreated phosphor; i.e., no In₂O₃ particles were apparent on the surface of the phosphor. Treatment with the 5 wt % In₂O₃ resulted in partial coverage of the phosphor with In₂O₃ nanoparticles. With increasing percentages of In₂O₃, the coverage of In₂O₃ particles became denser, with complete coverage realized at 10 wt % InCl₃. When aqueous solutions

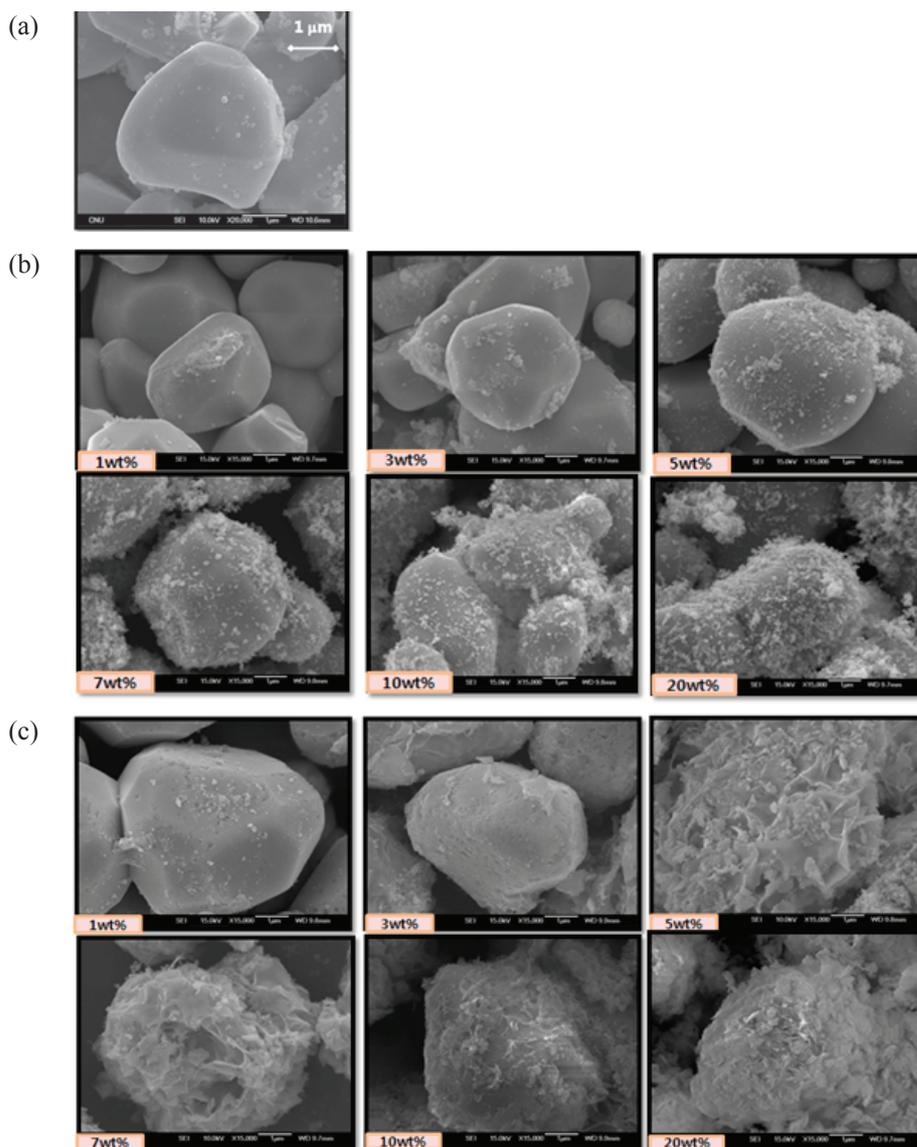


Figure 1. FE-SEM images of (a) uncoated, and (b) In_2O_3 nanoparticle- and (c) In_2O_3 film-coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors.

of InCl_3 were used, the resulting morphology of In_2O_3 coating differed from that observed with ethanolic solutions. In both solutions, the In_2O_3 coatings were accomplished by the hydrolysis of InCl_3 with NH_4OH . In the ethanolic solution, however, the polymerization *via* In-O-In network was very unfavorable, compared with the case in the aqueous solution. It might result in the nanoparticles instead of the film. As shown in Fig. 1, the surface of the phosphor was covered with a thin In_2O_3 film after treatment with 3 wt % InCl_3 in water. The thickness of the In_2O_3 films increased with increasing percentages of InCl_3 . These results demonstrated that the degree of In_2O_3 coverage on the red phosphor was proportional to the amount of the InCl_3 used in the deposition solution.

EDS spectrum was also measured to determine the relative surface composition of the In_2O_3 -coated surface phosphors and it is shown in Fig. 2. The results of the compositions on the In_2O_3 -coated phosphors are listed in Table 1. It can be found

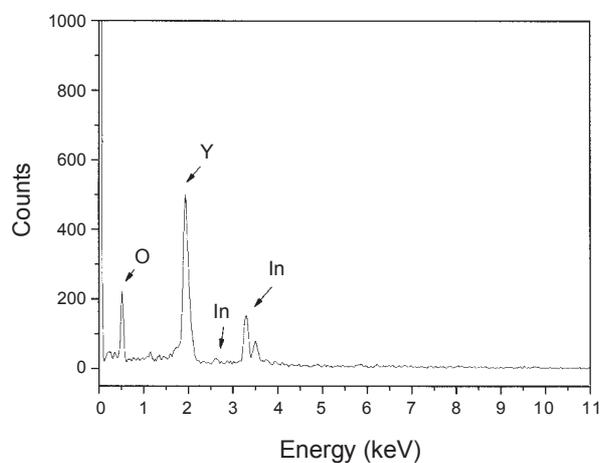
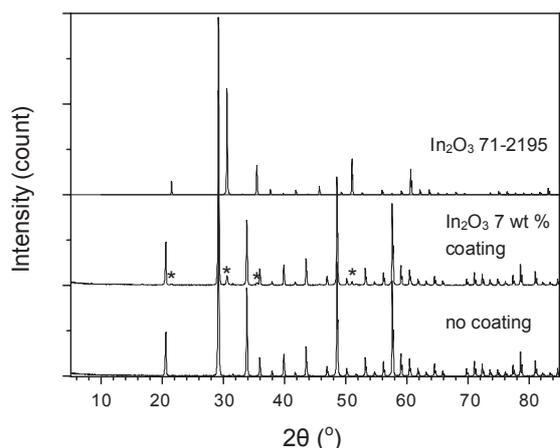
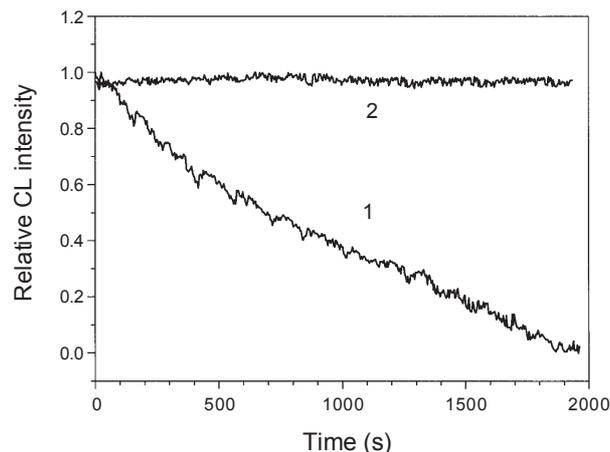


Figure 2. EDS spectrum of typical In_2O_3 -coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$.

Table 1. The element compositions of In_2O_3 -coated phosphors from EDS analysis

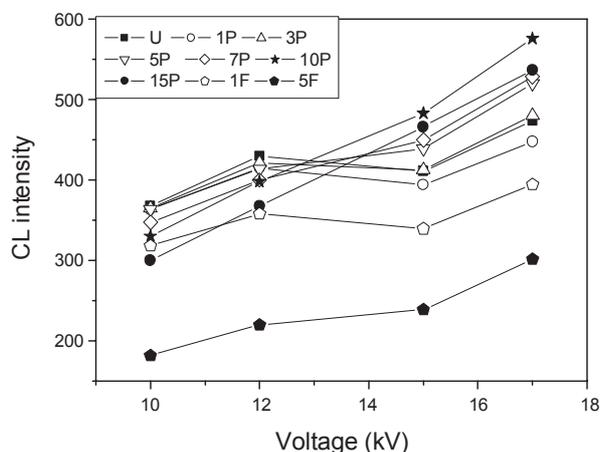
wt % Precursor	Nanoparticle (atomic %/wt %)			Film (atomic %/wt %)		
	O	Y	In	O	Y	In
1	74.2/33.75	24.43/61.79	0/0	77.6/38.4	22.4/61.7	0/0
3	78.6/39.7	21.1/59.1	0.34/1.23	76.7/37.2	23.3/62.8	0/0
5	76.0/35.8	22.3/58.4	1.7/5.8	79.5/40.8	19.4/55.3	1.1/3.9
7	71.8/31.0	26.2/62.8	2.0/6.2	77.3/37.5	20.9/56.3	1.8/6.1
10	73.2/32.1	23.3/56.6	3.6/11.3	79.8/40.9	18.5/52.8	1.7/6.3
15	78.0/37.7	17.6/47.3	4.4/15.1	77.4/36.9	18.5/49.1	4.1/14.0

**Figure 3.** XRD patterns of uncoated and In_2O_3 nanoparticle-coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors (the lines of In_2O_3 are noted by *).**Figure 4.** Relative CL intensities of (1) uncoated and (2) In_2O_3 nanoparticle-coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors. The concentration of the InCl_3 precursor solution was 10 wt %.

that the wt % composition of In increased with increasing the wt % of the precursor.

XRD patterns of both the uncoated and In_2O_3 nanoparticle-coated phosphor are shown in Fig. 3. No In_2O_3 peaks were detected with less than 3 wt % InCl_3 precursor. Above 3 wt % of InCl_3 , a characteristic peak of In_2O_3 became discernible at $2\theta = 30.6$.

CL properties. Previously, Cho and co-workers⁸ prepared a spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor using an aerosol pyrolysis method and measured its CL intensity. The CL intensity of the uncoated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor, when excited with an applied voltage of 400 V at a current density of $50 \mu\text{A cm}^{-2}$, decreased to 47% of the initial intensity after the first 10 min. In the current study, the aging of uncoated and the In_2O_3 -coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor was evaluated during excitation at an accelerating voltage of 17 kV and $1.57 \mu\text{A cm}^{-2}$. As shown in Fig. 4, the CL intensity from the uncoated phosphor during high-energy electron bombardment decreased by 94% after 2000 s. In contrast, the phosphor that had been treated with 10 wt % of InCl_3 in ethanol maintained a stable CL intensity for the same 2000-s duration, despite the incomplete nanoparticle coverage. In the 10 ~ 17 kV ($1.57 \mu\text{A}$) excitation voltage range, as shown in Fig. 5, the CL intensity of the uncoated phosphor gradually increased with increasing voltage with some fluctuation in linearity. The CL intensity profiles of phosphors treated 1 and 3 wt % concentrations of InCl_3 were very similar to those of the uncoated phosphor. Above 3 wt %, however, the amount of fluctuation in the CL data decreased and the slope of the CL

**Figure 5.** CL intensities of uncoated and In_2O_3 coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors measured in the high voltage range (U: uncoated, P: In_2O_3 nanoparticle-coated, F: In_2O_3 film-coated, digitals: wt % InCl_3).

intensity increased. At 10 kV, the CL intensity of the phosphor that had been coated with the 5 wt % solution of InCl_3 was almost equal to that of the uncoated phosphor. Increasing the voltage resulted in an increase in the relative CL intensity of the nanoparticle-coated phosphors. At 17 kV, the CL intensity of the coated phosphors increased by more than 10%. Phosphors treated with InCl_3 solutions above 7 wt % exhibited lower CL intensity than the un-coated phosphor at voltages up to 12 kV.

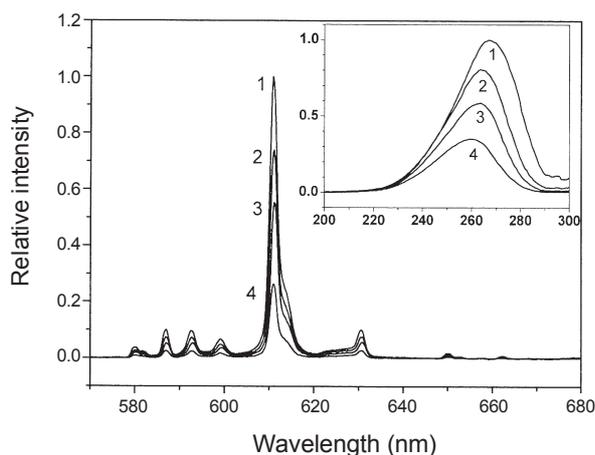


Figure 6. Luminescence spectra of uncoated and nanoparticle In_2O_3 -coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ excited at 264 nm (1: uncoated, 2: 1 wt %, 3: 3 wt %, 4: 5 wt % InCl_3). The strongest band at 610.8 nm corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions. Charge-transfer excitation bands for the 610.8 nm emissions from the uncoated and coated phosphors are inserted.

At 17 kV, however, the CL intensity increased substantially. The strongest CL intensity was observed at 17 kV with a phosphor that had been treated with the 10 wt % InCl_3 solution, representing a 22% enhancement over the CL of the uncoated phosphor. The CL intensities as a function of applied voltage for the 5, 7, 10 and 15 wt % coated phosphors were evaluated as $20.2 (\pm 4.1)$, $24.4 (\pm 2.9)$, $34.0 (\pm 2.4)$ and $33.6 (\pm 0.3)$ $\text{Cd m}^{-2} \text{V}^{-1}$, respectively. Fig. 5 shows that the CL intensity of phosphors coated with In_2O_3 films resulting from the aqueous deposition of InCl_3 was significantly less than that of the uncoated phosphor. For the phosphor treated with 1 wt % InCl_3 , the SEM image shows that only a small fraction of the surface was covered by the In_2O_3 film. However, this slight coverage was enough to reduce the CL intensity by about 13%.

The nanoparticle In_2O_3 -coating effect on the CL intensity is very extraordinary, compared with the case for the PL. Fig. 6 shows the PL spectra of uncoated and the nanoparticle In_2O_3 -coated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor, excited by the charge-transfer band ($\lambda_{\text{exc}} = 264$ nm). The PL intensity of the coated phosphor was significantly affected by the In_2O_3 nanoparticles: the PL intensity significantly decreased with increasing the amount of the In_2O_3 nanoparticles. For the electron-beam excitation, the In_2O_3 nanoparticles were very effective in reducing charge buildup on the surface of the insulating phosphor during high-voltage excitation to result in the beam penetrating into the deep inside of the phosphor.

Conclusions

A red phosphor composed of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was coated with In_2O_3 by immersing the phosphor into either an ethanol or aqueous solution of InCl_3 precursor with subsequent heat annealing. The morphology of the coating depended on the solvent used

in the precursor solution. Precursor deposition from ethanol resulted in partial coverage of the phosphor surface by In_2O_3 nanoparticles; the use of an aqueous solution resulted in multi-layered In_2O_3 thin films. Aging effects of the uncoated phosphor during excitation were profound; the CL intensity decreased by about 94% after 2000 s, presumably due to surface charging of the phosphor induced by high-energy electron bombardment. The CL intensity of both uncoated and coated phosphors was measured at excitation voltages between 10 and 17 kV. The In_2O_3 nanoparticles were very effective at stabilizing and enhancing the CL intensity, even at sub-monolayer coverage. In contrast, thin film coatings of In_2O_3 significantly reduced the CL intensity. From these results, the conclusion was drawn that surface modification of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with In_2O_3 nanoparticles would significantly improve the luminance of FEDs operating at voltages above 10 kV.

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